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RESEARCH REPORT

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A methodology has been developed for the determination of ashes to fiber and fibril content of particulate samples collected from the air. This report describes the effort on development of the analytical method and gives details of the method which includes sampling, beneficiation of asbestos fiber and fibril, and determination of total asbestos by a transmission electron microscopic technique. Included in the report are results of analyses of samples collected near a point source, in urban ambient air, and in a remote rural site.

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DEVELOPMENT OF A RAPID SURVEY METHOD OF SAMPLING AND ANALYSIS FOR ASBESTOS IN AMBIENT AIR

FINAL REPORT

Covering the Period
June 1969 through July 1971

Contract No. CPA 22-69-110

Prepared for: Environmental Protection Agency
Division of Atmospheric Surveillance

Project Director: W. M. Henry
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February 29, 1972

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February 29, 1972

Dr. Richard J. Thompson
Air Quality Analytical Laboratory Branch
Division of Atmospheric Surveillance
Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dear Dr. Thompson:

Ref. Contract CPA 22-69-110

Enclosed are twenty-five copies, including a reproducible master, of the Final Report on the above contract titled "Development of a Rapid Survey Method of Sampling and Analysis for Asbestos in Ambient Air". One copy of the Final Report has been forwarded to the Contracting Officer.

This Final Report, as required in the revised report schedule, is specified in the supplemental agreement dated November 6, 1971.

As nearly as possible, the changes as suggested by you have been incorporated in this final draft revision. The rough-draft copies were approved by you, subject to the revisions, by letter of January 21, 1972.

Very truly yours,

R.E. Heffelfinger

R. E. Heffelfinger
Associate Chief
Environmental and Materials
Characterization Division

REH:ng
Enc. (24 plus 1 reproducible)

cc: Vincent E. Mason
Contracting Officer
Durham Contract Operations
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MANAGEMENT SUMMARY

Contract CPA 22-69-110

"Development of Rapid Survey of Sampling and Analysis for Asbestos in Ambient Air".

Objective of Research Program

This program was initiated to develop a technique for determining total amounts of asbestos, including fibrils, in ambient air and to provide quantification of the concentrations of asbestos in various types of urban and rural air.

Significance of Research Results

The research results show that by the use of separation and enrichment techniques the total asbestos fibers and fibrils collected from ambient air can be identified and quantified using transmission electron microscopy. This is highly significant from a health point of view since prior art did not provide data on the smaller and more respirable fibers to which large portions of the population might be unwittingly exposed.

The air-analysis results indicate that asbestos concentration in ambient air may range from a few hundreths nanograms per cubic meter in remote areas to a few thousand nanograms per cubic meter near point sources.

How Sponsor Can Use Results

The Environmental Protection Agency will be able to use the techniques developed to study the concentration, sources, range, and persistence of total asbestos as an air pollutant. Such data will provide a firm basis, not now available, for epidemiological investigations and for better criteria and standards related to asbestos contamination in the atmosphere.

Future Effort

Additional research effort is outlined that will provide a more rapid and more automatic means for the analysis of air for asbestos. Also, more research effort is needed to provide particle-size-frequency information. However, the methodology as developed now can be used on collected samples to obtain additional data needed to set criteria standards.

ABSTRACT

A methodology has been developed for the determination of ashes to fiber and fibril content of particulate samples collected from air.

This report describes the effort on development of the analytical method and gives details of the method which includes sampling, beneficiation of asbestos fiber and fibril, and determination of total asbestos by a transmission electron microscopic technique.

Included in the report are results of analyses of samples collected near a point source, in urban ambient air, and in a remote rural site.

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DEVELOPMENT OF A RAPID SURVEY METHOD OF SAMPLING AND ANALYSIS FOR ASBESTOS IN AMBIENT AIR

by

R. E. Heffelfinger, C. W. Melton, D. L. Kiefer, and W. M. Henry

SUMMARY AND RECOMMENDATIONS

A methodology has been developed and demonstrated which is capable of determining total amounts of asbestos fibers and fibrils in air ranging from as low as fractional nanograms per cubic meter (ng/m^3) of air to several micrograms/m^3. The method involves the collection of samples on an absolute filter and provides an unequivocal identification and quantification of the total asbestos contents including fibrils in the collected samples.

The developed method depends on the trituration under controlled conditions to reduce the fibers to fibrils, separation of the asbestos fibrils from other collected air particulates (beneficiation), and the use of transmission microscopy for identification and quantification. Its validity has been tested by comparative analyses by neutron activation techniques. It can supply the data needed to set emissions criteria and to serve as a basis for assessing the potential hazard for asbestos pollution to the populace. The key to the method is the nearly complete separation of the asbestos from other air particulate matter and its uniform deposition on a microscope grid for observation and counting using an electron microscope.

Analyses of about 70 sample collections show that asbestos concentrations of ambient air range from a few tenths ng/m^3 in remote areas to a few thousand ng/m^3 near point sources.

The physiological process of inhalation and absorbance into body tissue is not well understood. Both large and small asbestos bodies have been found in persons afflicted with asbestosis and mesothemia. Perhaps the human body retains inhaled fibers intact or breaks them up, and thus their size may be physiologically insignificant. It would be desirable, therefore, to examine also the particle size distribution of asbestos (both fibers and fibrils) as it exists in the atmosphere. Experimental efforts do show that asbestos fibers collected from ambient air by cascade impaction are present on all stages of the impactor as agglomerates, fibers, and fibrils. While some estimates of particle size distribution are made in this report, the estimates are from preliminary experiments. Generally, it has not been possible to measure quantitatively the particle-size distribution of asbestos fiber agglomerates, fibers, and fibrils in the airborne condition.

Further effort is needed to provide for more rapid analyses and effort should also be directed toward continuous automatic monitoring. These efforts may include development of more rapid sample-preparation techniques for the electron microscope as well as development of optical-microscopic techniques, infrared techniques, and X-ray diffraction techniques. Each of these techniques would require beneficiation of asbestos.

Certainly, further effort is needed to obtain more data on particle size distribution and number.

INTRODUCTION

The relationship between exposure to asbestos dust and lung health problems has been the subject of much study and discussion[1,2,3], but no clear conclusions can be drawn, largely because of the lack of an analytical method for the determination of total asbestos. To provide a background for definitive epidemiological investigations concerned with pathology related to asbestos, and to set meaningful emission criteria, knowledge of the total concentration, sources, range, and persistence of asbestos as an air pollutant is required. To develop the capability for such a study, Battelle, working with Dr. Richard J. Thompson of EPA, has devised a technique for sampling and analysis for total asbestos fiber content including fibrils in particles collected from ambient air.

Prior to this study, the analytical technology for estimating the amount of asbestos fiber in air was dependable only for fibers visible by optical microscopic techniques. That procedure was useful for assessing the concentrations of asbestos in heavily loaded atmospheres such as are encountered by workers in asbestos-product industries and by insulation workers. However, the presence of asbestos fibrils (≈300 A in diameter) cannot be determined directly by such techniques. Fibrils are present in ambient air, particularly near point sources. Because of their very small size these can and do remain suspended in the atmosphere and are transported long distances. As evidence of this, there are documented cases of asbestosis in persons having no known direct contact with industrial production or use of asbestos products. Consequently, there was a great need for an analytical methodology for the quantitative measurement of all forms and sizes of asbestos in ambient air.

The goal of this program was to develop such a methodology.

OBJECTIVE

The research objectives for this program as spelled out by Battelle's proposal and by the contract scope are summarized as follows:

(1) Evaluate methods of sampling for particles in the range of 0.01 to 10 μm

(2) Investigate optical, physical, and chemical techniques to identify and measure asbestos fibers

(3) Develop beneficiation procedures to isolate and differentiate asbestos from other atmospheric particulate

(4) Identify mineralogical species of asbestos

(5) Quantify asbestos analysis procedure

(6) Verify feasibility of the developed procedure for possible routine use

(7) Analyze samples taken at remote and point source sites

(8) Document procedure.

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(1) Newhouse, M. L., and Thompson, H., "Mesothelioma of Plura and Peritoneum Following Exposure to Asbestos in London Area", Brit. J. Indust. Med., 22, 261 (1965).

(2) Selikoff, I. J., and Hammond, E. C., "Community Effects of Nonoccupational Environmental Asbestos Exposure", A. J. Ph., 58 (9), 1658 (1968).

(3) Thomson, J. G., Kaschula, R.O.C., and McDonald, R. R., "Asbestos as a Modern Urban Hazard", South African Medical Journal, 27, 77 (1963).

Previous Work by Battelle

The results described in this report are an extension of effort carried out by Battelle on a previous program under Contract PH-22-68-54.

In that program various means of detecting asbestos materials were employed utilizing the unique physical and chemical properties of asbestos. These methods included electron microprobe (EMP), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and light microscopy (LM) and are discussed in the sections below.

In addition optical emission spectrography methods, which depended on the unique chemical composition of asbestos, and X-ray diffractometry, which depended on the unique structural characteristics of asbestos, were investigated. However, these characteristics were buried in the makeup of particulate samples and were undetectable.

EXPERIMENTAL WORK

Raw Materials

The following five types of raw asbestos were purchased[4] for the purpose of making synthetic experimental samples:

Serpentine (chrysotile, fibrous, Quebec)

Amphibole (loose fibers, white, Quebec)

Amphibole (long fiber masses, gray, Montana)

Crocidolite (dark blue, fibrous, Transvaal)

Amosite (long fiber, gray, Transvaal)

These materials were examined petrographically to ensure that they were the types represented by the supplier.

In addition, a sample of "respirable" pure white Chrysotile was obtained from John Mansville and used in the developmental efforts. This material was identified by its morphological detail as shown by electron microscopy.

Detection and Identification of Asbestos Fiber and Fibril

Samples of three forms of asbestos, amosite, chrysotile, and crocidolite, were used in preliminary investigations to determine suitable means of detection and identification of asbestos. The investigations included the chemical properties composition and physical appearance of asbestos. In carrying out these studies it was realized that ambient air samplings would collect not only asbestos fibers and fibrils but other air particulates. These other air particulates either singly or in combination do contain elemental compositions similar to the asbestos mineral compositions and many also are of a fibrous nature grossly similar in appearance to asbestos. For these reasons it was concluded that the asbestos could not be determined as an aggregate but would require detection of individual fibers and fibrils.

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(4) Ward's Natural Science Establishment, Inc., Rochester, New York.

The samples which were examined in the preliminary study are listed in Table 1.

TABLE 1. ASBESTOS SAMPLES EXAMINED IN THE PRELIMINARY STUDY

Sample Designation	Asbestos Form	Treatment
1	Amosite	Ground to small particle size
4	Chrysotile	Ground to small particle size
5	Crocidolite	Ground to small particle size
6	Chrysotile	100 μ collected on membrane filter
7	Chrysotile	Low-temperature ashing (LTA)
8	Chrysotile	Low-temperature ashing (LTA) duplicate of Sample 7
9	Chrysotile	Ignited at 400 C
9a	Chrysotile	Ignited at 750 C
10	None	Deionized H_2O residue on membrane filter
11	Unknown	15-hour, low-volume air sample
12	Unknown	15-hour, low-volume air sample; subjected to LTA

Electron Microprobe Studies

Studies of the above samples showed that the electron microprobe (EMP) is capable of identifying asbestos fiber by its composition provided the fiber is large enough (->0.5 μm) and is isolated from other particles that may contain Si, Fe, Na, or Mg. However, because asbestos fibers and fibrils were found by other techniques to occur in sizes much smaller than 0.5 μm, the EMP was shown to be of limited value in the identification of asbestos in collected air samples.

Scanning Electron Microscopy Studies

The scanning electron microscope (SEM) permits rapid viewing and photography of materials and provides image resolutions down to about 100 A. Replicas are not required and, although a thin conductive coating frequently must be put on the surface of a sample, SEM offers a faster and more direct method for examining small particles than does electron microscopy.

Since SEM offers an approach which is supplementary and complementary to optical light microscopy and electron microscopy, it could serve as both a qualitative and quantitative method for estimating asbestos contents of ambient air samples. However, in the limited studies carried out on this program, this has not been the case. Ambient air samples have been examined both as collected on a membrane filter and after having been ashed. In both cases the SEM images have shown the fibers more as clumps or "piled up" and interwoven groups rather than as individual particles as seen in electron micrographs. The difference in resolution between the two techniques is accountable at least in part for this. However thus far it has not been possible to get good estimates of the amount of asbestos present by the use of SEM photographs alone.

This effort on the SEM also showed the SEM could not unequivocally distinguish between forms of asbestos.

Transmission Electron Microscopy

The samples listed in Table 1 were examined by transmission electron microscopy (TEM) by thin section techniques and transfer replicate techniques. For the thin section examination, the samples were imbedded in a commercially available epoxy mixture, Maraglas (available from Polyscience Inc.). Thin sections 750 A thick were cut on a Porter-Blum MT-1 microtome equipped with a Du Pont diamond knife.

The transfer replica was made by evaporating a carbon film over the surface of the filter bearing the asbestos and dissolving the filter in acetone to leave the thin carbon film supporting the asbestos fibers and fibrils.

The examinations showed that:

(1) The various forms of asbestos can be identified by their individual morphologies

(2) Crystallinity is a valid criterion for distinguishing between asbestos fiber and glass fiber although not necessary because of identification by morphology

(3) Morphology and crystallinity of asbestos fiber and fibrils are both affected by ignition at 750 C

(4) A magnification of the order of 30,000X is optimum for identification of asbestos.

Light Microscopy

Light microscopy techniques were examined only briefly as a technique for identification of asbestos because the diameter of many of the asbestos fibers and especially the fibrils are below the resolving power of the light microscope. Dark field and dispersion staining techniques were found capable of identifying fibers at sizes somewhat below the normal resolving power of the instrument but the methods were not suitably specific for unequivocal identification.

In summary, transmission electron microscopy is the only technique investigated that provided unequivocal identification of asbestos fiber as well as asbestos fibril material. TEM techniques were used throughout the remainder of the developmental program for asbestos identification.

Sampling

Sampling methodology selection was based on two criteria: (1) it must collect asbestos particles in the required range of 0.01 μm to 10 μm and (2) it must ultimately be suitable for use in the sampling network of EPA. The latter dictated that sampling be fairly simple and easy to perform and, if possible, require no complicated apparatus. The sampling techniques considered included cascade impaction, liquid impinging, and membrane filtration. The glass fiber filter now used in the EPA air sampling network was not considered because of the interferences introduced by glass fiber when it is present with collected asbestos fiber.

To permit the evaluation of sampling methods, samples of airborne particulates were collected near point sources, where asbestos would be expected to be a significant portion of the total particulate, and at locations where asbestos would be expected to be lower than near point sources. Tables 8 through 13 show the location, sampling techniques, and the amount of asbestos found in samples collected for this study.

Cascade Impactor

Since the cascade impactor collects particles according to aerodynamic size on its various stages, Battelle's objective was to determine whether asbestos fiber is selectively collected on certain stages. The collections were made directly on carbon-coated electron-microscope grids affixed to each of the six stages.

Examination by transmission electron microscopy (TEM) showed asbestos fiber and fibril on virtually every stage (e.g., Stages 1, 3, 4, 5, and 6). Electron micrographs from Stages 1 and 5 of the Cincinnati sample are shown in Figures 1 and 2. It is clear that asbestos fibers and fibrils are collected with no obvious selection according to size.

An implication of this finding is that total air samples are necessary for analysis rather than samples with a portion of the particulate removed by preimpaction. A study of the impactor samples revealed also that asbestos very often is collected as loosely agglomerated fibers and fibrils in association with other particulates. Further work with the cascade impactor to try to determine asbestos particle sizes is described in a later section.

All-Glass Liquid Impinger

The samples collected with the all-glass liquid impingers could have been examined for the presence of asbestos fibers by an otical-microscopic interference-contrast technique. Because of the large amount of nonasbestos particulate collected simultaneously, the technique was considered not applicable without beneficiation of asbestos. The interference-contrast technique also would not distinguish nonasbestos fibers or different mineralogical species of asbestos fiber.

Membrane Filters

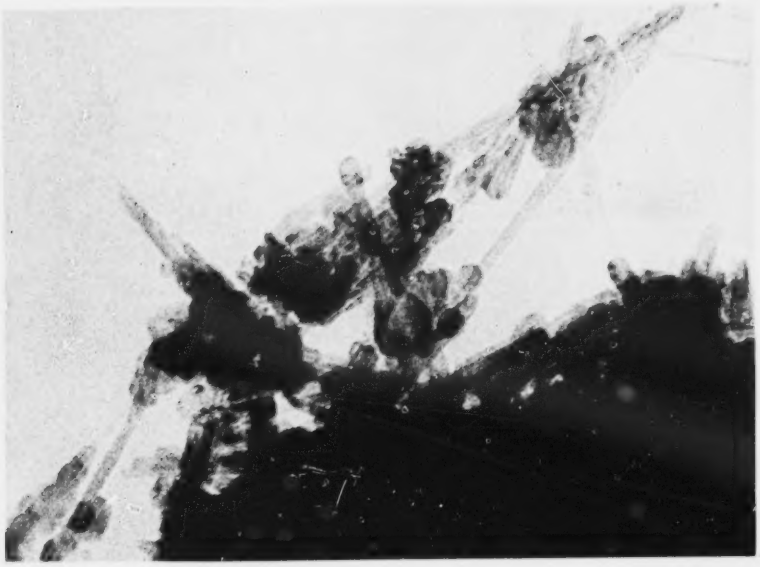
The membrane filters were evaluated by direct examination using a light microscope and by scanning electron microscopy (SEM) for their usefulness in available sampling apparatuses. Samples of various areas (from 25-mm circle to 30 x 30-cm square) were taken on 0.45-μm-pore-size Millipore filters (esters of cellulose), and on 0.45-μm-pore size Flotronics (silver). Direct examination of the membrane-filter samples by light microscopy and SEM proved fruitless because of the inability to detect asbestos fiber in the presence of larger amounts of other particulates and to resolve the smaller fibers and fibrils.

Ultimately, plastic membrane filters were found acceptable because of their low ash content, lack of fibers of any kind, and their adaptability to field sampling procedures.

Beneficiation

Initially, collections on membrane filters were prepared for electron microscopic examination by the transfer replicate technique on the sample as collected. It was obvious that the particulate sample, as collected, was so loaded that asbestos particles were obscured, or so light that the asbestos particles seen and counted were too few and too sparse to be statistically representative of the total sample. Figure 3 shows an electron micrograph of a sample as collected. It appeared, therefore, that a process was needed to (1) concentrate or beneficiate the asbestos particles and (2) provide for a means of redistributing the asbestos particles uniformly and in a countable frequency.

The first of these needs was accomplished by ashing, which removed organic particulate such as soot, and when necessary by centrifuging which removed inorganic particles which were large compared to the asbestos particles.



30,000X J17767

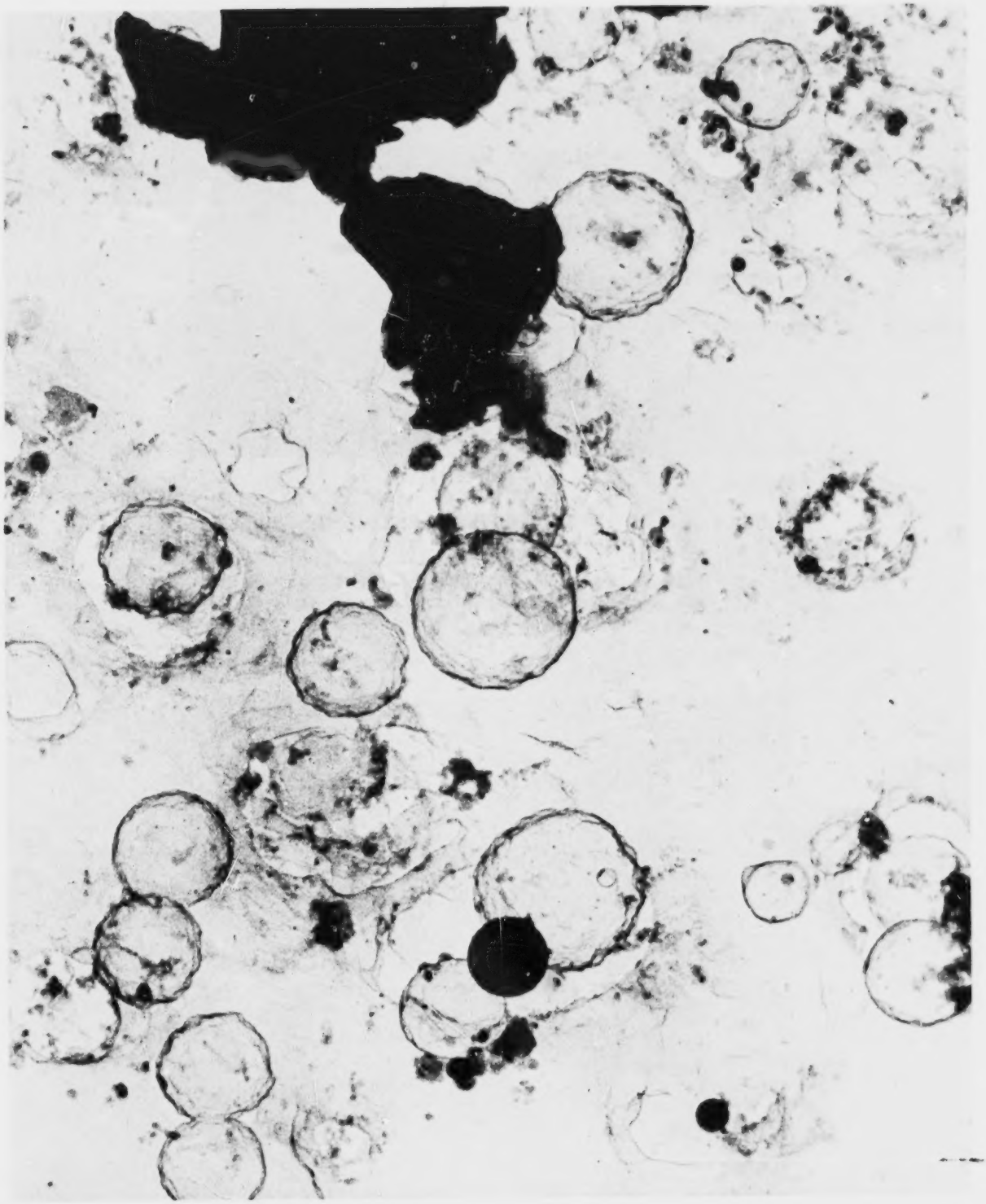
FIGURE 1. A CLUMP OF AGGLOMERATED PARTICLES PARTLY COMPRISED OF ASBESTOS (CHRYSOTILE)

This clump was collected at Stage 1 of the cascade impactor where particles aerodynamically equivalent to 16.0-μm spheres of water are collected.

30,000X J17802

FIGURE 2. ASBESTOS FIBERS COLLECTED AT STAGE 5 OF THE CASCADE IMPACTOR

This stage collects particles which are equivalent aerodynamically to 1.0 μm spheres of water.



57,000X J17092

FIGURE 3. ELECTRON MICROGRAPH OF A TYPICAL DEPOSITION OF AIR PARTICULATE FROM FILTERED AIR

The second of these needs was accomplished by ultrasonically dispersing the asbestos particulate in an aqueous media and refiltering the dispersed particulate. The refiltered asbestos particulate was then prepared for EM by the transfer replicate technique.

Low-Temperature Ashing of Collected Sample

Organic materials are eliminated by low-temperature combustion in oxygen. The ashing treatment removes about half the total interfering particulate material.

It was found that the low-temperature ashing (LTA) of the deposit on the membrane filter could best be done in an induction-coupled oxygen plasma at about 1-torr total pressure. If the collected sample and filter are ignited in air there is danger of sample loss because of the explosive manner in which the membrane filter burns. For the LTA ignition, the chance of physical loss of particulates from the oxygen draft is virtually eliminated by placing the sample in a Pyrex test tube with the open end in a position such that the oxygen plasma flows across the tube mouth normal to the axis of the tube. Possible contamination from the laboratory atmosphere is eliminated by using LTA, in which the atmosphere is tank oxygen.

The ash residue from the collected sample remains in the test tube, which is convenient for insertion into the ultrasonic bath that is necessary to break up agglomerates of particulates in order to provide a uniform deposit for the electron microscope.

The dry ash is suspended in water containing a surfactant (Aerosol OT) and is dispersed by ultrasonic energy.

Ultrasonification

Asbestos fibers are composed of fibrils of fairly constant diameter, but indefinite length. If the fibers are triturated they will be reduced to fibrils which will be of random lengths. If the energy used in the fiber-reduction process is controlled, the fibril lengths will be random, but of a reproducible but small range distribution of lengths. These fibrils could be considered alternate particles under fixed conditions. By trituration of a weighed known asbestos sample and an unknown asbestos-containing sample under controlled conditions, the fibril length distribution should be comparable in each sample. Ultrasonification has proven to be valuable for this process because of the repeatability of the energy utilized and the efficiency, as compared to other mechanical means, of trituration.

Centrifugation

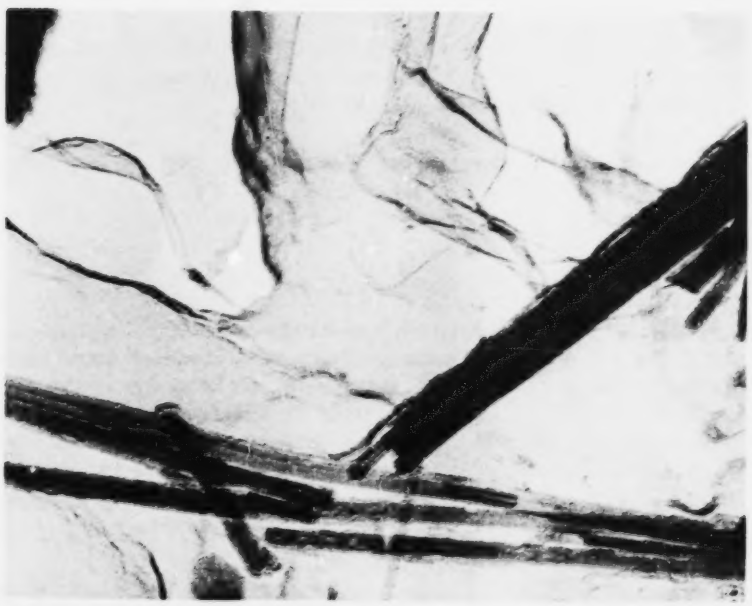
Unlike the asbestos, the fly ash and most of the other particulates appear to retain the same size before and after ashing and dispersion by ultrasonic treatment; therefore, centrifugation can be used for fractionation by size. The larger particles settle, while the smaller asbestos particles remain in suspension. The ultrasonically dispersed aqueous suspension of ashed sample is centrifuged at 900 g for about 20 minutes. The supernatant portion is then decanted and filtered on a plastic membrane filter.

The precipitation is repeated a second time. Additional aqueous surfactant solution is added to the residue precipitated by the first centrifugation in order to redisperse it and to recover any of the asbestos carried down with the precipitate. Examination of the material retained by the filter after the first centrifugation revealed the presence of most of the asbestos fiber plus some additional very fine fly-ash-type particles, which indicates good separation. It is estimated that centrifuging twice eliminated about 90 percent of the interfering particulates from most samples. Studies of synthetic standards show that approximately 80 to 90 percent of the asbestos fiber is recovered.

Dispersion and filtration from a selected volume of liquid onto a known filter area provide the advantage of allowing control of the amount of particulate deposited per unit area of filter. The amount is chosen to be best suited for electron microscopic examination. The amount per unit area is varied either by using an aliquot of the aqueously dispersed particulate or by varying the size of the filter area on which the particulate is finally deposited.

Any sample treatment, and especially the ultrasonic dispersal, alters the particulate so it is not observed in the electron microscope in the same condition as while airborne or even as sampled. The ultrasonic treatment disperses and dispenses the particulate matter and breaks the asbestos into shorter and finer particles, resulting in the formation of many individual fibrils of colloidal dimensions. It should be emphasized, however, that only a relatively small portion of the sample is actually examined by electron microscopy, so a uniform distribution is necessary to provide a statistically sound basis for analysis of the asbestos particulate by counting only a reasonable number of asbestos fibers and fibrils.

Figure 4 is an electron micrograph of separated fibrils.



60,000X J18308

FIGURE 4. ELECTRON MICROGRAPH OF A TYPICAL DEPOSITION OF SEPARATED FIBRILS

Investigations into other means of separating asbestos largely on the bases of their electrical properties and density were carried out. These experiments and results, described in Appendix A, were only partially successful.

Beneficiation Summary

Battelle's recommendation for beneficiation is to ash every sample but centrifuge only when necessary. According to recent experience, centrifugation is necessary only for a small fraction of the samples.

Assuming no prior knowledge on a sample, the amount to be taken for analysis must be arbitrary. Typically, 1/8 or 1/16 of the total sample or an amount that can be ashed at a low-temperature in a few hours has been taken. As detailed in the methodology, the ash is suspended in 100 ml H_2O and two aliquots are taken, 10 ml and 90 ml.

If asbestos cannot be counted in either aliquot because of either too much nonasbestos particulate or too little asbestos particulate, then centrifugation will be useful. In that case a larger aliquot of the sample should be taken to be treated in the extra step of centrifugation.

Quantification

Experience showed that TEM at 30,000X is necessary to identify the asbestos fiber as to mineralogical type and also to distinguish asbestos fiber and fibrils from any other particulate that may have an axial ratio of 10 to 1 or more.

Because TEM operates at relatively high magnifications, only a small area can be examined in a reasonable length of time, and the asbestos fiber and fibril must be dispersed very uniformly. Satisfactory dispersal is carried out as described above by application of ultrasonic energy to an aqueous suspension of ashed air particulate containing added surfactant. Subsequent filtration of such a suspension provides a uniform dispersal on the collecting media. Standards must be treated similarly.

Standards

Ordinarily, in making an analysis of particles by optical microscopic techniques, the particles in an aliquot of a sample can be counted and the count can then be related to the total sample, provided the particles are counted in the as-collected condition. However, after disruption and dispersal of the asbestos by application of ultrasonic energy to obtain a uniform deposit, a particle count is meaningless by itself. The count needs to be related to a standard.

Since there were no standards available for asbestos in air, synthetic standards were made up. The synthetic standards were made up by dispersing and suspending known weights of asbestos in aqueous-surfactant media and making quantitative volumetric transfers of the suspensions to Millipore filters.

For example, suspensions of asbestos containing 1.0, 0.1, 0.01, and 0.001 μg/ml of asbestos were made up. 1 ml of each of the four suspensions was then filtered through each of four Millipore filters. Each Millipore filter then contained known amounts of asbestos and were treated as an air sample. Figure 5 is an analytical working curve which gives the relationship of fiber count per 200 mesh screen opening to μg asbestos per 17-mm diameter filter disk.

The dispersion and suspension of asbestos fiber was promoted by the addition of Aerosol OT (dioctyl sodium sulfosuccinate) and ultrasonic energy to break down the larger asbestos particles into particles of fibrillar dimensions. The suspensions were useful for only two days because of the fairly rapid dissolution of the fiber in the aqueous media.

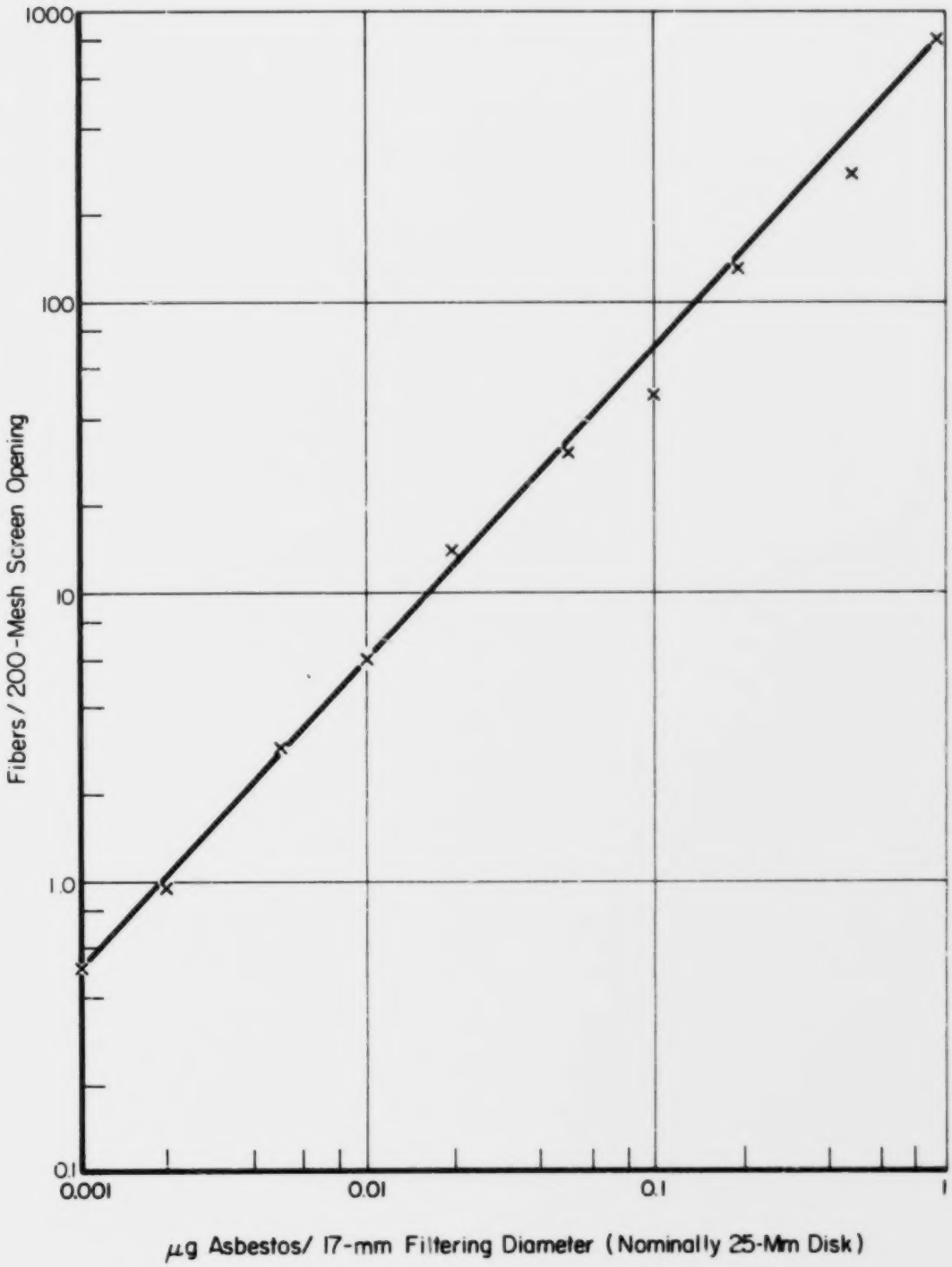


FIGURE 5. PLOT OF FIBER COUNT PER 200-MESH SCREEN OPENING VERSUS MICROGRAMS ASBESTOS PER FILTER DISK

Standardization is successfully carried out using only asbestos. However, to demonstrate this, standards were prepared that contained asbestos and other particulate such as pulverized sea sand, ignited air particulate, and fly ash.

The results for these standards when carried through the procedure for preparing and analyzing air samples agreed with the results for standards prepared with asbestos only.

RESULTS

Description of the Methodology for the Analysis of Asbestos in Air

The methodology is described in detail so that other laboratories, even though not familiar with the techniques employed, could follow the procedure and obtain satisfactory data.

A. Sampling

Virtually any sample collected on plastic-membrane filter material is applicable. The procedure and apparatus listed below are useful for relatively small samples (<100 m^3 depending on particle loading in the air sampled).

(1) Collect air samples on Millipore Type HA 47 mm, 0.45-μm-pore-size filter disks held in a clean-room monitoring filter holder (such as Millipore Cat. No. XX 50 047 40) supplied with a 5-liter/min limiting orifice

(2) Connect the above filter holder to a vacuum pump capable of maintaining a pressure drop of at least 8 psi at a flow rate of 5 liter/min

(3) Carry out sampling for the desired monitoring period

(4) Record volume of the air sampled

(5) Removed filter from filter holder and store in clean petri dish.

B. Sample Preparation

(1) Handle specimen in a clean laboratory environment, class 100 or better.

(2) Take half of filter (Step 5 of A), fold and put in the bottom of Pyrex test tube (1.5 cm x 9 cm). (See Note 1.)

(3) Put test tube in a low-temperature asher for 2 hours or until sample is completly ashed. (Low-temperature asher, such as Tracerlab-LTA 600.)

(4) Remove test tube, and add 5 ml of filtered deionized water and 2 ml of 1.0 percent Aerosol OT (Fisher So-A-292).

(5) Treat ultrasonically for 5 minutes in ultrasonic generator (such as Branson Ultrasonic Corporation – Sonogen T-32) to disperse and suspend the ash.

(6) Transfer the dispersed sample to a 10-ml volumetric flask; dilute to 100 ml.

(7) Tap out 10 ml while the flask is subjected to ultrasonic energy to assure dispersal, and filter through a 25-mm-diameter, 0.45-μm-pore-size filter. (See Note 2.) The filter funnel must be cylindrical (not tapered) so the suspended particles will deposit uniformly over the filter surface. Filter the remaining 90 ml above as a standby in case the 10-ml deposit is so sparse that a count cannot be made.

Note 1. The portion of a filter taken to process is arbitrary. A second portion may need to be selected to adjust for the amount of particulates finally deposited for the microscopic examination.

Note 2. Use filtering apparatus supplied by the Millipore Corp. Cat. No. XX 10 025 00, or equivalent, connected to a laboratory aspirator or vacuum pump.

(8) If the extraneous particulate to asbestos ratio is so high that a count cannot be made, take another portion of the sample, carry the new portion of the sample through Steps B-1 and B-5, and centrifuge sample at 500 to 1000 g for 20 minutes. Filter supernatant fluid through 25-mm-diameter, 0.45-μm-pore-size filter. (See Note 2.) Resuspend the reside and again centrifuge for 20 minutes and again filter the supernatant on the same filter.

C. Preparation of Specimen for Electron Microscopy

(1) Vapor deposit ≈200 A layer of carbon over the ashed air sample distributed uniformly on Millipore filter from Step B-7 or B-8 above.

(2) Cut out a 5 x 5-mm piece of filter bearing the redistributed ashed and carbon-coated airborne particulates.

(3) Dissolve the cellulose acetate Millipore filter substrate using a petri dish approximately half filled with acetone.

(4) Aspirate the carbon film bearing the ashed, redistributed, airborne particles into a medicine dropper along with a few drops of the acetone used to dissolve the Millipore filter.

(5) Hold the medicine dropper vertically until the carbon film falls to the opening of the medicine dropper.

(6) Deliver a drop of acetone containing the carbon film to the surface of water held in another petri dish (about half full).

(7) Pick up the now flattened and floating carbon film from the surface of the water on a 200-electro-mesh electron-microscope copper support grid.

D. Examination of Specimen in the Electron Microscope

(1) Place specimen in electron-microscope specimen holder and examine systematically for asbestos particles at a magnification of 30,000X with a 100-kv beam.

(2) Count fibers per grid opening on at least five openings to obtain data on average number of fibers per opening.

E. Preparation of Standards

(1) Simulate the sample conditions by ultrasonically suspending known quantities of asbestos (1.0, 0.1, 0.01, and 0.001 μg) in about 0.5 percent Aerosol OT solution and then collecting on membrane filters.

(2) Dry filtered preparation and ash the preparation in the low-temperature asher for 2 hours.

(3) Resuspend the ash in 5 ml of filtered deionized water plus 2 ml of 1 percent Aerosol OT and subject the resulting suspendion to ultrasonic dispersal treatment for 5 minutes as was done in Step B above.

(4) Refilter on a 25-mm Millipore filter and allow to dry.

(5) Go through the entire procedure for "Preparation of Specimen for Electron Microscope" and "Examination of Specimen in the Electron Microscope" (Steps C and D).

(6) Figure 5 gives a working curve relating fiber count to amount of asbestos.

F. Analysis of Microscope Data

(1) Compare fibers per opening for samples with comparable data for standards to obtain micrograms of asbestos per sample.

(2) Translate the micrograms of asbestos per sample into micrograms of per cubic meter.

Note 3. Mention of a commercial product does not constitute endorsement by EPA. Equivalent equipment from other manufacturers may be equally suitable.

Reliability of the Method

Comparison of Results From the Method and Neutron-Activation Analyses

A check on the quantitativeness of the method was carried out through experiments with neutron-activation analyses. For this experiment, neutron-activated asbestos was sampled by cascade impaction and each stage of the impactor was analyzed by radioassay techniques. Four of the stages were analyzed also by the TEM method developed during this program. The results of these analyses are shown in Tables 2 and 3.

These experiments demonstrate that (1) independent analyses of the same sample provide agreement within 30 percent, (2) asbestos apparently is distributed in various identifiable size ranges, and (3) the Battelle cascade impactor appears to be capable of collecting asbestos according to size.[5]

Radioassay. The activation experiments which produced the above data are summarized here.

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(5) Stober, W., Flachabart, H., and Hochrainer, D., "The Aerodynamic Diameter of Latex Aggregates and Asbestos Fibers", Staub-Reinhalt Luft, **30** (7) (July, 1970).

TABLE 2. RADIOASSAY OF ASBESTOS ON IMPACTOR STAGES

Stage	Asbestos Collected After Wet and Dry Dispersion in Air, μg	
	Wet Dispersion	Dry Dispersion
1	0.1	0.1
2	0.1	0.1
3	0.5	1.7
4	8.3	0.7
5	34.0	2.9
6	17.6	5.7
7	4.7	12.5
Final	2.3	2.4

TABLE 3. COMPARISON OF RESULTS OF ANALYSIS OF ASBESTOS ON IMPACTOR STAGES BY ELECTRON MICROSCOPY AND RADIOASSAY

Stage	Asbestos, μg		Difference, %
	Electron Microscopy	Radioassay	
4	11.6	8.3	+29
5	40.0	34.0	+15
6	20.8	17.6	+15
7	4.0	4.7	- 18

In order to determine the effect of neutron radiation on asbestos, a 100-mg sample of Johns-Manville No. 3778-29-1 chrysotile asbestos sealed in a quartz tube was irradiated for 7 days in a neutron flux of about 1×10^{13} n/cm^2/sec. The major long-lived radioisotopes produced during the irradiation are listed below with their nuclear properties.

Isotope	Half-Life	Significant Decay Characteristics	Quantity Produced, μCi/μg of asbestos
^{45}Ca	163 days	β-0.25 Mev	3.4×10^{-4}
^{45}Sc	84 days	β-0.357 Mev γ-0.889, 1.12 Mev	1.4×10^{-5}
^{59}Fe	45 days	β-0.475 Mev γ-0.19, 1.1, 1.29 Mev	1.1×10^{-5}

Two experiments were performed in which the irradiated asbestos was introduced into air by different techniques. In the first experiment, the activated asbestos was dispersed in 0.1 percent Aerosol OT solution at a concentration of 20 μg/ml. Ten ml of the asbestos suspension (200 μg asbestos) was atomized into a 4-foot-diameter sphere over a period of about 1.5 hours. Sampling was performed with a seven-stage Battelle impactor sampler during and for 1.5 hours following the sample injection. The flow rate through the sampler was 12.5 l/min.

In the second experiment, a 2.8-mg sample of dry irradiated asbestos was atomized into the 4-foot-diameter sphere in one burst. Sampling with the Battelle sampler at 12.5 l/min was initiated about 15 minutes after sample injection and continued for 70 minutes. About 34 and 7 percent of the added asbestos was recovered in the sampler in Experiments 1 and 2, respectively, showing that asbestos was lost in the system, as expected.

Radioassays and Results

The Millipore filters from the seven impactor stages and the final filter (Millipore, 0.45-μm pore size) were radioassayed with a Beckman Widebeta, low background, gas-flow proportional-counting system. Counting times of 50 to 100 minutes were used, which resulted in counting errors of less than 1 percent for most samples. Asbestos standards were prepared by filtering 1-ml aliquots of the 0.1 percent Aerosol OT solution of the irradiated asbestos used in the first experiment through a 0.22-μm Millipore filter. The filtrate was checked for radioactivity to assure that all the asbestos was retained on the filter. The specific activity (counts/min/μg) of duplicate standards agreed within 2 percent. The quantities of asbestos on the impactor stages and the final filter were determined by comparison of their activity (counts/min) to the specific activity of the standards (counts/min/μg). The weights of asbestos found in the two experiments are summarized in Table 2.

Replication

The repeatability of the methodology was checked by analyzing several of the samples in duplicate and triplicate.

The replicate data is given in Table 4.

The data shows an agreement between replicates of the order of ±10 to 20 percent except in one instance where the agreement is about ±50 percent.

TABLE 4. REPLICATE RESULTS OF ANALYSES OF SELECTED AIR SAMPLES

Sample Identification	Asbestos, $\mu g/m^3$	Report Value, $\mu g/m^3$
Lockland Post Office 9/3/70	280, 260	270.
Wyoming Municipal Bldg. 9/3/70	29, 37, 32	33.
Lincoln Heights City Hall 9/3/70	28, 40	34.
Lincoln Heights, Mathews, and Dixie 9/3/70	12, 38	25.
Lockland Post Office 1/14/71	110, 86	98.
Lincoln Heights City Hall 1/14/71	130, 117	124.
Lockland Post Office 1/21/71	7900, 7200, 9700	8200.
A31	0.115, 0.102, 0.147	0.12
A34	0.094, 0.119, 0.106	0.10
A43	0.028, 0.024, 0.026	0.03

Particle Size/Frequency Measurements

On the bases of the demonstrable features of collection and analyses, project personnel proceeded to collect air samples by cascade impaction near a point source in order to obtain size-frequency-distribution information on a real air sample. Samples were collected at distances of 1 and 2 miles downwind from the point source, with results shown in Table 5.

The total of 0.109 μg for the 1-mile sample, as shown in Table 5, was obtained during a 2-hour sampling at 12.5 l/min. The asbestos collection rate, therefore, amounted to about 0.07 $\mu g/m^3$. Simultaneously with the impactor sample, a sample was taken on 0.45-μm-pore-size Millipore filter material to represent a total sample collection. This was carried out to assess the overall efficiency of the cascade impactor. The results from analysis of the total sample likewise showed a 0.07-$\mu g/m^3$ concentration for asbestos.

TABLE 5. ANALYSIS OF EACH STAGE OF CASCADE-IMPACTOR SAMPLES TAKEN AT 1 AND 2 MILES DOWNWIND FROM A POINT SOURCE

	μg Asbestos/Stage	
Stage	1 Mile From Point Source	2 Miles From Point Source
1	0.004	0.006
2	0.04	0.009
3	0.025	0.007
4	0.012	0.002
5	0.018	0.005
6	0.005	--
7	0.005	--
Total	0.109	--

Ordinarily, the cascade impactor is backed up with a glass-fiber filter to collect material that is not impacted. Glass fiber is not applicable for analysis and the flow rate through the Millipore filter is too low to pass the required flow through the impactor stages. Therefore, analysis of a backing filter was not applicable.

Since the amount of asbestos found in the cascade impactor agrees with the amount in the total collection, virtually the total mass has been collected by the impactor. Although the cascade impactor collects the total *mass* of particulate efficiently, there may still be a significant *number* of particles in the 0.01-μm range that have not been collected.

In further efforts to determine particle size, an asbestos point source was sampled by the cascade impactor for short times (20 and 4 minutes) so the particle loading on each stage would be sparse. Isolated, single asbestos particles were thus collected and found by electron microscopy on Stages 4, 5, and 6. Figures 6, 7, and 8 are electron micrographs of the particles. Data on approximate size of the particles are given in Table 6.

TABLE 6. SIZE OF ASBESTOS PARTICLES FOUND ON STAGES 4, 5, AND 6 OF A CASCADE-IMPACTOR AIR SAMPLER

Stage	Calculated Range of Sizes of Particle as Stokes Diameter, μm	Measured Dimensions, μm	Calculated Volume, μm^3	Equivalent Diameter[(a)], μg	Calculated Particle Wt[(b)], μg
4	2-4	11 x 0.6	4	1.97	10×10^{-6}
5	1-2	8 x 0.36	1	1.25	2.6×10^{-6}
6	0.5-1	1.3 x 0.15	0.03	0.38	0.08×10^{-6}

(a) Calculated as spherical particles.
(b) Using density of chrysotile as 2.5 g/cc.

In order to demonstrate how these types of data might be used to determine particle-size distribution, the following calculations were made.

The weight data in Table 6 was used to estimate weights of individual asbestos particles collected on each stage of the cascade impactor. Using the data from Stage 4 as a reference and assuming that the weight will vary by a factor of 8 (2^3) these estimated weights are given as follows:

Stage	Microgram/Particle
1	5×10^{-3}
2	6×10^{-4}
3	8×10^{-5}
4	1×10^{-5}
5	1×10^{-6}
6	2×10^{-7}
7	2×10^{-8}

The above data then provide a means of estimating the number of particles collected by each stage of the impactor sample listed in Table 5. These calculated particle numbers are shown in Table 7.

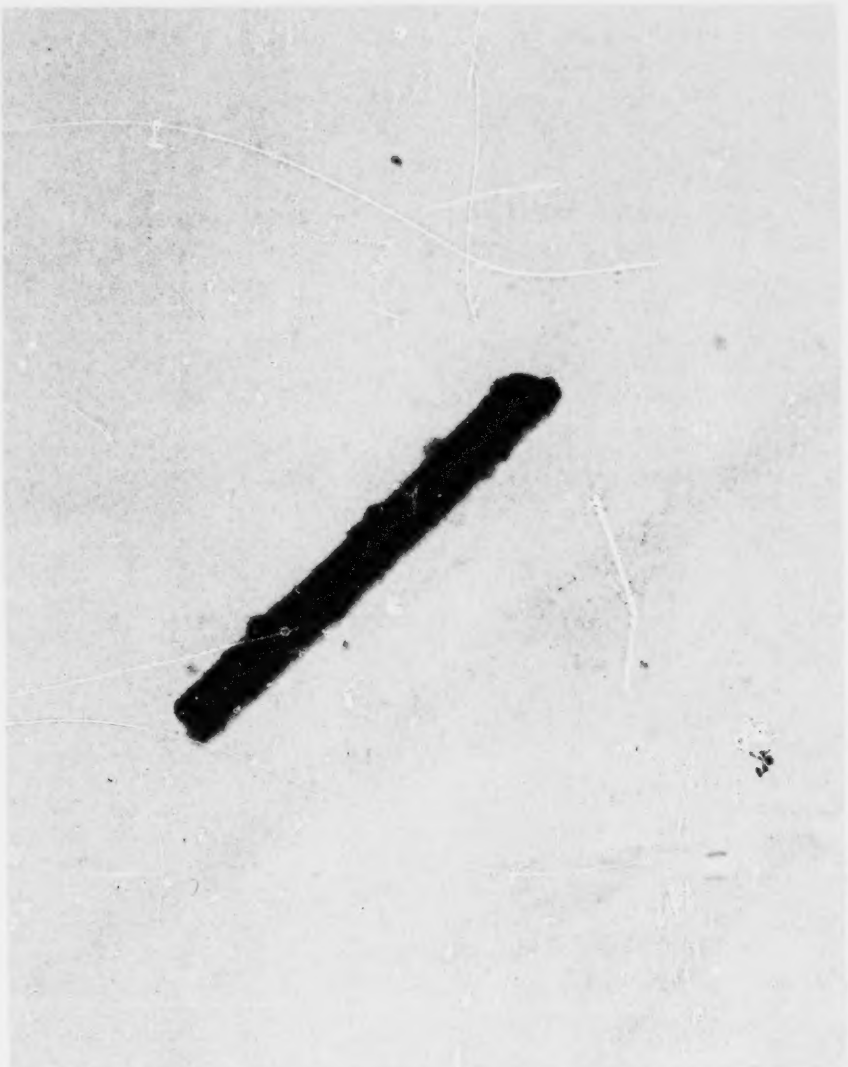
These data give an idea of the order of magnitude of particle-number distribution, but more effort is needed to obtain supporting data and to assess particle-size distribution from various sources and for ambient air at various locations.

22,000X J19751

FIGURE 6. ELECTRON MICROGRAPH OF SINGLE PARTICLE OF ASBESTOS COLLECTED ON STAGE 4 OF THE BATTELLE CASCADE IMPACTOR

22,000X J19752

FIGURE 7. ELECTRON MICROGRAPH OF SINGLE PARTICLE OF ASBESTOS COLLECTED ON STAGE 5 OF THE BATTELLE CASCADE IMPACTOR



57,000X J19753

FIGURE 8. ELECTRON MICROGRAPH OF SINGLE PARTICLE OF ASBESTOS COLLECTED ON STAGE 6 OF THE BATTELLE CASCADE IMPACTOR

TABLE 7. ESTIMATED PARTICLE NUMBER FOUND ON EACH STAGE OF THE CASCADE-IMPACTOR SAMPLE SHOWN IN TABLE 5

Stage	Size Collected (Stokes Diameter), μm	Total Particles	Percent (by Number)	Cumulative Percent
1	>16	0.8	0.0003	100.00
2	8-16	60.0	0.02	99.99+
3	4-8	300.0	0.1	99.97
4	2-4	1,200.0	0.5	99.8
5	1-2	18,000.0	7.5	99.3
6	0.5-1	20,000.0	8.3	91.8
7	0.25-0.5	200,000.0	83.5	83.5

Data From Various Sites

The data from analysis of some 80 samples which were mostly supplied by EPA are shown in the following tables.

Table 8 contains the results for the analyses of Urban Samples.

Table 9 contains the results of analyses of Site Source Samples.

Table 10 contains the results of analyses of samples from a nonurban remote site.

Tables 11, 12, and 13 show the results of analyses of miscellaneous samples. Table 11 shows the results of analyses of the various tages of samples collected by cascade impaction. This data provides an estimate of asbestos particle-size distribution in air near a site source.

Table 12 gives the results of analyses of samples collected for preliminary studies. The data are not necessarily significant.

The data in Table 13 are result of analyses of air samples taken from the exhausts of various vane pumps.

DISCUSSION AND CONCLUSIONS

By utilizing the methodology as detailed in this report, it is possible to obtain a reliable analysis for asbestos in air. The time required per sample depends mainly on whether or not the sample needs beneficiation by centrifugation. The analytical results can be expressed in terms of weight of asbestos per unit volume of air or per unit weight of sample, whichever is most applicable. On the basis of cross-check analyses, the data appear to be reliable within ±30 percent of the stated amount. The precision of the measurement appears to be of the order of ±10 percent as determined by triplicate analyses of several samples.

TABLE 8. ANALYSES OF URBAN SAMPLES SUPPLIED BY SPONSOR COLLECTED ON REINFORCED PLASTIC MEMBRANE MATERIAL

(Collection Volume About 200 m^3)

Sample Identification	Asbestos, ng/m^3
Dayton M502 4-8-69	3.8
Dayton M508 7-9-69	5.6
Dayton M508 10-6-69	11.0
Dayton M508 1-2-70	0.5
Dayton 3167 4-8-70	4.0
Dayton 3167 7-4-70	0.4
Dayton 3178 10-7-70	5.1
Houston 2987 4-8-70	6.0
Houston 2993 7-4-70	4.0
Houston 2998 9-20-70	4.0
Houston 2997 10-7-70	4.0
Pittsburgh 2544 4-8-70	2.0
Pittsburgh 2544 7-4-70	8.0
Pittsburgh 2544 10-7-70	3.0
San Francisco 2330 4-8-70	40.0
San Francisco 2332 7-11-70	1.5
San Francisco 2339 10-14-70	3.0
Washington, D. C., No. 1 3rd quarter	40.
Washington, D. C., No. 2 3rd quarter	1.6
Washington, D. C., No. 1 4th quarter	4.0
Washington, D. C., No. 2 4th quarter	2.6

TABLE 9. ANALYSES OF SITE SOURCE SAMPLES – SAMPLES COLLECTED BY SPONSOR AT A POSITION DOWNWIND FROM A SITE SOURCE NEAR CINCINNATI, OHIO

(Plastic Membrane Filter Material)

Sample Identification	Location Relative to Point Source	Air Vol, m^3	Asbestos, ng/m^3
Lockland Police Station 9/3/70	3/4 mi. NE	0.6	62
Lockland Police Station 9/3/70	3/4 mi. NE	1.87	170
Lockland Police Station 9/3/70	3/4 mi. NE	1.87	100
Lockland Post Office 9/3/70	3/4 mi. NNE	1.87	180
Lockland Post Office 9/3/70	3/4 mi. NNE	1.81	270
Wyoming Municipal Bldg. 9/3/70	5/8 mi. NNW	1.87	24
Wyoming Municipal Bldg. 9/3/70	5/8 mi. NNW	1.19	33
Lincoln Heights City Hall 9/3/70	1-1/4 mi. N	0.8	34
Lincoln Heights City Hall 9/3/70	1-1/4 mi. N	1.87	70
Lincoln Heights City Hall 9/3/70	1-1/4 mi. N	1.87	11
Lincoln Heights, Mathews and Dixie 9/3/70	1-7/8 mi. N	1.87	17
Lincoln Heights, Mathews and Dixie 9/3/70	1-7/8 mi. N	1.87	25
Blank		–	4 (total on filter)
Lockland Post Office 1/14/71	3/4 mi. NNE	2.8	570
Lockland Post Office 1/14/71	3/4 mi. NNE	1.4	98
Lockland Post Office 1/14/71	3/4 mi. NNE	1.4	<60
Lincoln Heights City Hall 1/14/71	1-1/4 mi. N	3.7	124
Lincoln Heights City Hall 1/14/71	1-1/4 mi. N	3.7	<20
Lincoln Heights, Mathews and Dixie 1/14/71	1-7/8 mi. N	3.7	600
Lincoln Heights, Mathews and Dixie 1/14/71	1-7/8 mi. N	3.7	<20
Lockland Post Office 1/21/71	3/4 mi. NNE	1.4	8200
Lockland Post Office 1/21/71	3/4 mi. NNE	1.4	3400
Lockland Post Office 1/21/71	3/4 mi. NNE	3.1	5200
Lincoln Heights City Hall 1/21/71	1-1/4 mi. N	3.4	1800
Lincoln Heights City Hall 1/21/71	1-1/4 mi. N	5.8	915
Lincoln Heights City Hall 1/21/71	1-1/4 mi. N	2.3	200
Lincoln Heights, Mathews and Dixie 1/21/71	1-7/8 mi. N	3.7	<20
Lincoln Heights, Mathews and Dixie 1/21/71	1-7/8 mi. N	7.5	150
Lincoln Heights, Mathews and Dixie 1/21/71	1-7/8 mi. N	3.7	160

TABLE 10. ANALYSES OF SAMPLES COLLECTED FROM NONURBAN – REMOTE AIR, SAMPLES COLLECTED NEAR FRANKFORT, KENTUCKY

(Plastic Membrane Filter Material)

Sample	Air Vol, m^3	Asbestos, ng/m^3	Results of Replicate Analyses, ng/m^3
A 31	2512	0.12	0.115, 0.102, 0.147
A 34	2191	0.10	0.094, 0.119, 0.106
A 43	2186	0.03	0.028, 0.026, 0.024

TABLE 11. SAMPLES COLLECTED BY THE BATTELLE CASCADE-IMPACTOR NORTH (DOWNWIND) FROM POINT SOURCE NEAR CINCINNATI, OHIO (FEBRUARY 16, 1971)

(2-Hour Collection at 12.5 Liter/Min (1.5 m^3)

Stage	Stokes Diameter[(a)], μm	Asbestos, ng
	1 Mile From Point Source	
1	>16	4
2	8-16	40
3	4-8	25
4	2-4	12
5	1-2	18
6	0.5-1	5
7	0.25-0.5	8
	2 Miles From Point Source	
1	>16	6
2	8-16	9
3	4-8	7
4	2-4	2
5	1-2	5
6	0.5-1	–
7	0.25-0.5	–

(a) Diameter of particle of unit density which would be collected on the particular stage.

TABLE 12. SAMPLES COLLECTED FOR PRELIMINARY STUDIES

(Collection on Membrane and Paper Filter Material)

Sample	Source	Asbestos, ng/m^3
27097-2-1	Urban	5.0
27097-2-6	Urban	0.5
27097-2-7	Point source	4.0
27097-1-6	Point source	3000.
27097-2-7	Point source	1000.
27097-2-8	Point source	4000.
27097-20-1	Urban	5.
27097-2-2	Rural	2.
New York		0.3
Phoenix		0.07
San Francisco		0.4
San Diego		0.5
St. Louis		0.4
Newark, Ohio or New Jersey		0.3

TABLE 13. VANE-PUMP SAMPLES SUPPLIED BY SPONSOR

(Collection on Membrane Filter)

Sample Identification	Asbestos, ng/sample
M-182 asbestos vane	150
M-183 carbon vane	60
M-184 lub vane	400
M-185 carbon vane	120
M-187 lub vane	150
M-188 carbon vane	250

Asbestos fibers are composed of fibrils of fairly constant diameter, but indefinite length. If the fibers are triturated they will be reduced to fibrils which will be of random lengths. If the energy used in the fiber-reduction process is controlled, the fibril lengths will be random, but of a reproducible but small-range distribution of lengths. These fibrils could be considered alternate particles under fixed conditions. By trituration of a weighed known asbestos sample and an unknown asbestos containing sample under controlled conditions, the fibril length distribution should be comparable in each sample. Ultrasonification has proven to be a valuable experimental tool for this process.

While it would be useful for input to health-effects studies to obtain data in terms of particle number, this method cannot provide such data. However, as discussed in previous sections, some data were generated that show that particle-size distribution can be estimated. More effort in that direction would be necessary to provide useful data.

All analyses results are given in nanograms per cubic meter. Except for the data shown in Table 12, all data are reported with a confidence of ±30 percent. The data in Table 12 were generated before the reproducible technique now established had been firmly determined, and less confidence is placed in these preliminary findings.

The data in Table 9 show some sample collections where asbestos was not found and for those samples a "less than" value is given. These data appear to be in error because other samples taken at about the same time and place show significant asbestos content. Analysis in triplicate of the samples where asbestos was not found confirmed these results so it is felt that these results may represent a sampling or meteorological anomaly. A lower detection limit could be obtained by adjustment of the sample preparation procedure.

The value of 8200 ng/m^3 obtained for the sample taken at Lockland Post Office on January 21, 1971 (Table 9) appears to be high. This value appears to be valid in that triplicate analyses of the sample gave 7,900, 9,000, and 7,200 ng/m^3.

FUTURE WORK

Further research effort on methods for the determination of asbestos in air should include the following:

- Improvement of the current method in terms of analysis speed
- Development of optical-microscopic, infrared-absorption, or X-ray diffraction techniques
- Further investigation of particle-size distribution
- Development of optical methods aimed at continuous monitoring.

Future work aimed at the improvement of the existing electron-microscopic method for the analysis of asbestos and the development of more rapid asbestos monitoring methods is most important. Representative specimen preparation and the time required for the analysis of a sample are of prime concern. Consequently, developmental effort should emphasize these two factors. Development of more rapid and effective separation and concentration of the asbestos fractions should be investigated. With highly effective methods for separating and concentrating the asbestos fractions, other optical, infrared, and diffraction techniques may become feasible.

After beneficiation, the concentrated asbestos fibers may be measured by employing the optical microscope coupled with specimen preparation which exploits optical interference to render visible

asbestos fibers and fibrils which in ordinary specimen preparations would escape detection. In this method, fibers whose diameters are well below that size which is resolvable by optical microscopy are made visible by multiple-beam interferometry. Some preliminary experiments using this approach for specimen preparation have shown promise.

Another approach to the detection of fibers suspended in fluids is a technique termed streaming birefringence. It is based on the fact that a fiber particle will become aligned with its long axis parallel to the flow of a fluid, and when numbers of crystalline birefringent fibers are so aligned in the field of a polarizing microscope between crossed Nicols, the light is depolarized and the presence of fibers becomes evident. This method was used, before electron microscopy was developed, to demonstrate the rodlike shape of the tobacco mosaic virus particle which is ≈150 A in diameter but sometimes as long as 2,000 A (0.2 μm).

It is envisioned that it would be possible to use two polarizing microscopes with a detector on each to implement a null method to selectively detect the contribution of fibrous structures to the depolarization of the polarized light. It is also envisioned that the sample could be recycled for a period of time to obtain an integrated signal attributable to the presence of asbestos.

Since asbestos exhibits characteristic infrared absorption and X-ray diffraction, these techniques might prove effective with proper sample treatment, including asbestos beneficiation.

Finally, because of the significance to health-effects studies, it is important to continue study on determination of particle-size distribution.

This effort would be an extension of the effort described in this report, and attempts would be made to describe and compare various types of air such as urban, rural, and remote, as well as air inside public buildings.

APPENDIX A

STUDIES OF BENEFICIATION OF ASBESTOS BY DIFFERENCES IN ELECTRICAL PROPERTIES AND DENSITY

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Studies of beneficiation show that the distinctive difference between the separated asbestos and the precipitated residue is mainly the shape and size of the particles in the two fractions. Length-to-diameter ratio may be 40 or more for the fibers and is probably 4 or less for the fly ash and dust in the remainder. No consistent chemical differences exist because both fractions are predominantly siliceous materials. Surface properties, as indicated by interfacial charge sign or charge density, zeta potential, or isoelectric point are, therefore, similar.

Electrical polarization is the feature most responsible to the difference in shape factors noted above. The term polarization is used in a loose sense to include a variety of effects induced by the separation of unlike charges at an interface.

It is well known that electrical charges tend to concentrate at an interface between two materials or phases in contact, because of the abrupt change in physical and chemical properties in passing across the boundary. Such an interface is provided when either needlelike asbestos fibers or blocky particles are suspended in a liquid. Assuming that both types of particles are suspended together in the same liquid in an electrical field, forces can be postulated which tend to affect the long fibers more than they do the blocky particulates. If properly applied, these forces can favor migration of the fibers to the electrodes and their attachment to the electrode surface.

A d-c field is probably preferable to an a-c field because the d-c field favors polarization of the charges on the suspended particles. The fibers will undergo greater polarization along the fiber axis and will tend to line up parallel to the field, with the ends pointed toward the electrodes. Charge separation will tend to cause migration toward the nearest electrode. Although charges will polarize, both on fibers and on other particulates, the effect is much stronger on the fibers, so fiber movement is also theoretically more rapid.

Charge polarization is likely to have a stronger influence on agglomeration than it does on migration. Both fibers and blocky particles will tend to remain together, after random contact from thermal or Brownian movements. Because of the pattern of polarization, charge separation causes the fibers to line up preferentially head to tail into longer filaments. Blocky particles also tend to aggregate but without so much preference for straight chains. Their aggregates may become large enough to settle out; however, separation by gravity depends upon the shape of the agglomerates.

With this experience as background, dielectric separation, electrophoretic separation, magnetic separation, and separation by the Beckman Continuous Particle Electrophoresis (CPE) instrument were then investigated.

Dielectric Separation

A method described by Rosenholtz and Smith[6] for separating various minerals according to dielectric constant (σ) was utilized. Their work indicated that a mineral powder such as chrysotile suspended in a liquid could be attracted selectively to two needlepoint electrodes immersed in a liquid having a lower dielectric constant than that of the suspended material. Conversely the suspended mineral

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(6) Rosenholtz, J. L., and Smith, T. T., "The Dielectric Constant of Mineral Powders", The American Mineralogist, **21**, 115-120 (1936).

particles were reported to be repelled from the needles when the liquid has the higher dielectric constant. In their work, Rosenholtz and Smith employed mixtures of carbon tetrachloride (σ = 2.24), ethyl alcohol (σ = 33.7), and water (σ = 81) to cover a wide range of σ values. In Table 1 of that report, over 150 minerals are shown as having been concentrated by the method, including chrysotile with a dielectric constant of about 33.7.

For the work at Battelle, a small unit similar to the one described by Rosenholtz and Smith was assembled. The cell was a small circular glass vessel about 2 cm deep. Both electrodes were bright platinum wire. To investigate their observation that the dielectric constant of chrysotile was greater than 33.7, a 10-mg portion of chrysotile was dispersed ultrasonically in 100 ml of ethyl alcohol. A portion of the liquid containing the dispersed asbestos was introduced into the glass cell, and separation was attempted at 220 volts ac. Separation could be observed under a low-power microscope and the asbestos fibers appeared to be flocculated around each of the two electrodes. They were not strongly attached, and about 60 percent of the fibers fell off when the electrodes were gently lifted from the solution. During the run, the concentration of asbestos fibers around each of the electrodes appeared to be a loosely flocculated mass. The results of this investigation were not encouraging because an excessive amount of effort would be required to work with available amounts of particulate in collected samples.

Electrophoretic Batch Separations

In two attempts to concentrate chrysotile by an electrophoretic batch method the cell used was a circular glass jar about 5 cm in diameter and 5 cm deep. The platinum screen electrodes had a submerged area of about 1.2 cm square in the electrolyte. A power source of 0 to 500 volts dc was utilized. To determine the collecting ability of the unit, the cell was charged with 10 mg of ultrasonically dispersed chrysotile in 100 ml of methyl alcohol and the separation was attempted. At 500 volts, the chrysotile flocculated, and these flocs appeared to stream from the vicinity of one electrode to the other electrode. After about a half hour, the flocks had concentrated on the positive electrode. When the electrodes were gently lifted from the methyl alcohol, about half the fibers fell from the positive electrode.

A second run was made with the modification that 60 mg of fly ash was added to the 10-mg charge of chrysotile. Again the chrysotile was found to be concentrated on the positive electrode. The fly ash appeared to have settled to the bottom of the glass cell. The positive electrode with most of the adhering chrysotile was lifted carefully from the cell. A microscopic examination of the attached fibers showed them to be relatively free of fly ash. While these two methods appeared to separate chrysotile somewhat, separations of microgram amounts of asbestos appeared to require too much time and cost; consequently, further efforts on these methods were abandoned.

Continuous Particle Electrophoresis

Effort on other programs with the Beckman continuous particle electrophoresis (CPE) instrument indicated that it could operate in the microgram range. Consequently, the capability of the CPE was examined in some depth.

Preliminary investigations with asbestos and other particulates indicated that the behavior of asbestos alone in the CPE is satisfactory in that asbestos was distributed in a reasonably narrow band. However, some other particulates of interest are also distributed over the same general band. Subsequently, air samples that had been ashed, suspended, and centrifuged (as described above) were utilized in the CPE instrument to determine whether effective beneficiation could be obtained. A portion of suspended centrifuged material to serve as a control was filtered on a 17-mm-diameter 0.45-μm-pore-size Millipore filter and a second portion was processed through the CPE.

Operating conditions were:

(1) Curtain buffer B-2

(2) pH 8.6

(3) 0.001 molar

(4) Flow rate, 20 ml/min

(5) Voltage gradient, 30 volts/cm

(6) Sample feed rate, 50 μl/min

(7) Cell coolant flow rate, 250 ml/min at 10 C.

The CPE cell effluent was collected in 48 separate fractions. Previous determinations of the electrophoretic mobility of asbestos indicated that it should be collected in Tubes 24, 25, and 26. The contents of these tubes plus Tubes 23 and 27 were filtered separately on 3-mm-diameter 0.45-μm-pore-size Millipore filters. These filters plus the 17-mm filter (not CPE processed) were counted by electron microscopy. No values were obtained for Tube 23 as it contained too many extraneous particles to see any asbestos. Also, the samples from Tube 27 could not be counted because of interference from an unexplained plastic film. The observed asbestos-fiber counts per screen opening for the remaining samples (Tubes 24, 25, and 26) were corrected so as to be equivalent in terms of filter area and volume of the control sample.

The corrected values for Tubes 24, 25, and 26 were 28, 73, and 17 asbestos particles per screen opening, respectively. The total of the three, 118, compares well with the value of 100 asbestos particles per screen opening obtained on the portion of the control sample not processed by CPE. The data indicate that little if any asbestos would have been found in Tubes 23 and 27 and that essentially complete recovery of the asbestos was obtained. Tube 25 contained 62 percent of the asbestos found. Most of the nonasbestos particles were collected in Tubes 23 and below, while the fractions containing the asbestos were relatively free from the extraneous particles.

It has been calculated that the centrifuged asbestos samples were enriched by factor of 5 after the additional CPE treatment. These results are promising, since the CPE conditions were arbitrarily chosen and operating parameters should be expected to improve with further work. However, in light of the acceptable and useful enrichment by centrifugation alone, it appears that only in rare cases would separation by both centrifugation and CPE be justified.

Density Separation of Asbestos From Other Materials

One of the more constant physical properties of asbestos is specific gravity and this property might be useful to separate it from other airborne materials by selective sedimentation according to densities. The use of two solutions having densities slightly above and slightly below the density of asbestos could be used to separate all materials, including the asbestos, with densities in the range between the two solutions.

To determine the practical feasibility of such a density separation for chrysotile (specific gravity ≈ 2.5) solutions were made of carbon tetrachloride (specific gravity = 1.585) and 1-, 1-, 2-, 2-tetrabromoethane (specific gravity = 2.964) having densities of 2.697 and 2.406 g/cm^3. Chrysotile should settle out in the less-dense solution and float in the other.

Initially, problems were encountered because of the tubular and flocculated form of the chrysotile. The fiber clumps tended to remain suspended for long lengths of time (usually several days) before the fibers became sufficiently wetted and all air bubbles were released. In order to avoid the problems of air entrapment the fibers were dispersed in the fluid under a vacuum. This procedure was quite satisfactory in dispersing flocculated asbestos and indicated that the chrysotile density was within the range from 2.4 and 2.7 g/cm^3.

In order to determine the effects of other particulate matter on the density separation process, ground chrysotile and A.C. Test Dust, mixed in the ratio 1:20 were dispersed in water using an ultrasonic agitator, filtered and then dried into a cake. Small amounts of this caked mixture were then dispersed into the solutions. The test dust behaved much the same as the asbestos indicating a density in the range 2.4 to 2.7 g/cm^3. One consistent problem was the tendency of the asbestos to form flocs in the solutions. This occurred when the concentration was as low as 1 mg of the particle mixture dispersed in 20 ml of solution.

Again, as with the electrophoretic work, it appeared as if finding optimum conditions for density separations would require a depth of experimental work not feasible under the project effort and no further work was done.

APTD-0965

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June 2, 1972

Dr. Richard J. Thompson
Air Quality Analytical Laboratory Branch
Division of Atmospheric Surveillance
Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dear Dr. Thompson:

Contract No. CPA22-69-110 PB-209477

This letter is to correct errors found in the Final Report dated February 29, 1972, on the above contract titled "Development of a Rapid Survey Method of Sampling and Analysis for Asbestos in Ambient Air".

The corrections are as follows·

(1) On page 18, Table 4, the columns headed "asbestos, $\mu g/m^3$" and "Report Value, $\mu g/m^3$" should read "Asbestos, ng/m^3" and "Report Value, ng/m^3", respectively.

(2) On page 19, Table 6, the column headed "Equivalent Diameter, μg" should read "Equivalent Diameter, μm".

Very truly yours,

R E Heffelfinger

R. E. Heffelfinger
Associate Chief
Environmental and Materials Characterization Division

REH:ees

Airmail

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